

(54) BEAD POLYMERISATION PROCESS

(71) ICI AUSTRALIA LIMITED

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(57) Claim 1. A process of incorporating non-polymeric particulate matter into a polymeric matrix which process comprises dispersing the non-polymeric particulate matter by a polymeric dispersant which is a copolymer prepared from a first component consisting of at least one monomer selected from the group consisting of vinyl aromatic hydrocarbons, and a second component consisting of at least one monomer selected from the group consisting of tertiary-nitrogen-containing vinyl monomers and vinyl-trialkylloxysilanes, in a medium comprising an organic phase comprising one or more vinyl monomers selected from the group consisting of styrene, substituted styrenes, and vinyltoluenes, and an aqueous phase containing a suspension stabilizer, and a cross-linking agent followed by the addition of a polymerization initiator.

2. A process according to claim 1 wherein the nonpolymeric particulate matter comprises magnetic particles.

17. Polymeric beads in a size range from 1 to 1 000  $\mu\text{m}$  comprising non-polymeric particulate matter and prepared by the process of any one of claims 1 to 16.

PROCESS FOR COMPOSITE POLYMER BEADS

## TECHNICAL FIELD

This invention relates to polymeric composites which are useful for the separation of small quantities of material from solution. In particular it relates to processes for the manufacture of polymeric material containing non-polymeric particulate matter.

The incorporation of particulate matter, such as for example magnetic particles, into polymeric resin beads to facilitate the handling and uses of these resins in ion exchange processes is well known. The particle-containing resins utilize the discovery that when finely divided ferromagnetic-containing ion exchange adsorbents are flocculated by magnetic forces of a suitable strength and agitated in the liquid to be treated, they still exhibit the high rates of adsorption appropriate to the original resin bead size but have the mechanical characteristics normally associated with larger resin beads. In another application ferromagnetic-containing resin beads may be used in mixed beds with other non-ferromagnetic beads and conveniently separated as desired, by the application of a magnetic field.

In addition to these ion exchange resin applications, magnetic particles have also been incorporated in composite adsorbents containing common adsorbing materials such as activated carbon which is used extensively throughout the chemical and process industries. It is typically used in the form of carbon black, graphite, or charcoals. Other materials with suitable adsorbing properties are the various naturally-occurring clays, for example, fuller's earth, and other mineral powders. Examples of the latter include quartz, silica gel, titanium dioxide, bauxite, zeolite and many metallic oxides.

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In this approach the composite adsorbent material typically comprises adsorbent particles and magnetic particles embedded in a porous matrix of organic polymeric material, the porosity of the matrix being such as to allow small molecules of molecular weight up to several hundred to enter freely into the interstitial structure of the matrix but to exclude large molecules of higher molecular weight whereby the composite material functions selectively to adsorb dissolved materials from solution. The inclusion of magnetic particles enables the composite adsorbents to be easily and rapidly separated from the solutions being treated even when those solutions contain other suspended particulate matter.

#### BACKGROUND ART

Conventional ion-exchange resins and composite adsorbents have suffered from a number of disadvantages.

First, there has been the risk of interaction between the magnetic particles and the components of the system in which the ion exchange resins or composite adsorbents have been employed. This is a particularly serious problem with the porous composite adsorbents referred to above. Many of the common magnetic materials, such as ferrites, cannot be readily used at a pH below 7 and are rapidly degraded at a low pH.

Secondly, it has been very difficult to avoid "flushing" of the particulate matter during the preparation of the resin or composite adsorbent bead.

"Flushing" refers to the tendency of the particle to leave the polymer during the formation of the bead. The particles frequently are completely excluded from the forming bead or concentrate and protrude from the outer surfaces of the bead. Where attempts have been made to encapsulate magnetic particles in a protective coating

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prior to incorporation in a resin or composite adsorbent, flushing has also been a problem.

A further problem relates to the processes of manufacturing ion exchange resins. Frequently it is  
5 desired to prepare polymeric beads and by subsequent reaction schemes to introduce onto these beads functional groups which will provide the desired ion exchange function. When magnetic particles are incorporated  
10 into the beads the range of possible subsequent chemical reactions of the polymeric bead matrix can be severely limited by the susceptibility of the magnetic material to attack. For example, for the important class of cross-linked styrene based resins key processes such as chloromethylation and sulphonation with chlorosulphonic  
15 acid or oleum cannot be used.

#### DISCLOSURE OF INVENTION

It is an object of our invention to provide a process of preparing polymeric beads containing particulate matter such as magnetic material, and which  
20 do not suffer from the disadvantages described above.

Accordingly we provide a process of incorporating  
non-polymeric particulate matter into a polymeric matrix, which process comprises dispersing the non-polymeric particulate matter by a polymeric dispersant  
25 in a medium containing one or more vinyl monomers and a cross-linking agent, and adding a polymerization initiator.

The nature of the polymeric dispersant and of the vinyl monomers is critical. Many dispersants and  
30 monomers are unsuitable and lead either to a porous polymeric matrix through which reagents may diffuse to attack the non-polymeric particulate matter, or to flushing of the non-polymeric particles from the forming polymer leaving the particles unprotected.

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The polymeric dispersants used in the process of our invention are copolymers prepared from two or more vinyl monomers. At least one monomer is selected from vinyl aromatic hydrocarbons, such as styrene and the vinyltoluenes. This monomer or groups of monomers forms the major component of the copolymer and is preferably from 80 to 97% of the copolymer on a molar basis.

At least one monomer is selected from the group consisting of tertiary-nitrogen-containing vinyl monomers and vinyl oxysilanes. Typical examples of this group of monomers are 2-vinylpyridine, 4-vinylpyridine, methyl dimethylaminomethacrylate, vinyltrimethoxysilane, and vinyltriethoxysilane. Monomers chosen from this group preferably comprise 20 to 3% of the copolymer on a molar basis.

The most preferred copolymers are styrene/4-vinylpyridine, styrene/2-vinylpyridine and styrene/vinyltriethoxysilane. The molecular weight range of the preferred copolymer is 10 000 to 30 000.

The vinyl monomers used to prepare the polymeric matrix are vinyltoluenes and styrene, optionally substituted. Substituted styrenes may include, for example, polyfluorostyrene but the preferred monomer is styrene. Two or more of these monomers may be used in combination.

Suitable crosslinking agents for the preparation of polymers from these monomers can be selected by those skilled in the art. Typical crosslinking agents are divinylbenzene, unsaturated polyesters, and triallyloxyethane. Divinylbenzene is the preferred crosslinking agent when the vinyl monomer is styrene.

Generally a catalyst is added with the crosslinking agent to promote the crosslinking. Appropriate catalysts are well known to those skilled in the art, for example in the case of divinylbenzene crosslinking agent, benzoyl peroxide may be employed.

In the process of our invention the polymeric dispersant is used to disperse the non-polymeric particulate matter in a media containing the vinyl monomers and the crosslinking agent. On addition of the catalyst the vinyl monomers polymerize and form a matrix enclosing the non-polymeric particles. By adjusting the speed of stirring and the proportion of reagents it is possible to produce particles coated with a thin protecting layer of polymer or composites of several particles embedded in a polymer matrix bead.

A wide range of non-polymeric particles may be incorporated in polymeric matrixes by the process of our invention, for example, magnetic materials, inorganic oxides and silicates, minerals and pigments. While some of these materials, for example, titanium dioxide, have previously been incorporated into polymeric matrixes by conventional dispersants it is a particular feature of the process of our invention that a wide range of magnetic materials can be readily and effectively incorporated into polymers.

Furthermore the nature of the magnetic material that can be incorporated by the process of our invention is not narrowly critical. Typical magnetic materials are iron and alloys of iron and metals such as for example, cobalt, nickel, manganese, molybdenum, and aluminium, iron-silicon alloys, magnetic ceramics and ferrites. Suitable ferrites include the naturally occurring magnetite ( $\text{Fe}_3\text{O}_4$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), jacobsite, franklinite, magnesioferrite, and magnetoplumbite. Chromium dioxides may also be used.

In a preferred embodiment of our process the non-polymeric particles are pre-coated with the polymeric dispersant prior to formation of the cross-linked polymeric coating.

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## BEST MODE OF CARRYING OUT THE INVENTION

The weight ratio of the polymer forming components to the non-polymeric particulate matter is adjusted to avoid too high a proportion of non-polymeric particles leading to incomplete covering of the non-polymeric materials, or too low a proportion for the particular application, eg, too little magnetism where magnetic particles are being incorporated. High levels of the non-polymer particles can also lead to a thick paste where the non-polymeric particles are difficult to disperse.

Preferably the weight ratio of non-polymeric particles to the polymeric dispersant is in a range from 12:1 to 5:1 while the weight ratio of polymeric dispersant to monomers is in a range from 1:5 to 1:20. When the process is used to encapsulate individual magnetic particles in a protective coating prior to incorporation of the protected magnetic particles into ion exchange resins or composite adsorbents, the weight ratio of magnetic particles to polymer coating is preferably close to unity.

In the embodiment where the non-polymeric particles are coated with polymeric dispersant in a preliminary step before the main polymerization step, this dispersant is conveniently that used in the subsequent polymerization step. This pre-coating of the particles with polymeric dispersant is more effective if heat is applied, for example by refluxing the non-polymeric particles in a solution of the dispersant in a solvent inert to the particles such as xylene. After refluxing the solvent is removed by evaporation. For this pre-coating step the weight ratio of polymeric dispersant to particles may be in the range of 5:1 to 30:1 preferably in the range of 8:1 to 16:1.

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In a preferred embodiment of our process the polymerization is carried out with an organic phase containing the monomers and an aqueous phase containing a suspension stabilizer, such as polyvinylalcohol. It is  
5 important to wash the coated particles after the polymerization step to remove this stabilizer and thus avoid difficulties in the subsequent incorporation of the coated particles into ion exchange resins and composite adsorbents.

10 The weight ratio of organic phase to aqueous phase is typically in the range from 1:5 to 1:20, preferably in the range of 1:10 to 1:15. The size of the coated particles is influenced by the apparent  
15 viscosity of the aqueous phase. Viscosity is largely determined by concentration and for polyvinylalcohol a useful concentration range is 4.5-5.5% w/w, with the addition of 10-40% w/w calcium chloride. Coated  
20 particles in the size range from 1 to 1 000  $\mu\text{m}$  can readily be prepared, the larger size requiring a calcium chloride concentration near 10%.

The preferred size is determined by the application to which the coated particles are put. Composite adsorbents, for example, are typically beads of  
25 approximate diameter 200-300  $\mu\text{m}$ , and the size of coated magnetic particles incorporated into such adsorbents must be such as to allow adequate packing into the beads. The desired coated magnetic particle size is  
30 therefore 1-15  $\mu\text{m}$  and this can be achieved in the above organic phase/aqueous phase embodiment of our process when about 30% w/w calcium chloride is used. If the  
35 magnetic material is initially of a larger particle size, it may be milled in the polymerization medium prior to the addition of the polymerization catalyst or initiator. This milling is also advantageous in ensuring  
that the individual particles are thoroughly wetted



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with dispersant.

Polymer bead size is influenced by the viscosity of the aqueous phase, the stirring speed, and the time of stirring. Optimum conditions can be readily  
5 determined for particular magnetic materials and polymers by those skilled in the art. The choice of temperature is to some extent influenced by the nature of the catalyst initiators used, for example, 70-80°C with benzoyl peroxide, and 65-70°C with azo-bis-butyronitrile.

10

#### INDUSTRIAL APPLICABILITY

One of the applications of the process of our invention is the preparation of coated ferromagnetic particles and composite adsorbents containing said  
15 particles, wherein the ferromagnetic particles are resistant to attack by components of the system being treated with the composite adsorbents. There are some acid-resistant magnetic materials available, for example the "Metglas" amorphous alloys ("Metglas" is a trademark of Allied Chemical Company, New Jersey), but none of  
20 these have the high magnetic permeability required for particles incorporated into composite adsorbents.

The preferred magnetic materials for this application are the ferrites, and particularly magnetite and maghemite. These materials are less dense than the  
25 alloys and are readily dispersed in the polymerization medium. They are also easily milled, for example, in the embodiment of our invention where the particles are milled in the polymerization medium prior to the addition of the polymerization initiator.

30

Ferromagnetic particles prepared by the process of our invention are stable in the pH range from 14 to 2. In contrast to unprotected magnetic material they can be readily used in aqueous solutions of acids, such as acetic acid. Even below pH 2 some protection is



provided.

A further application for the coated magnetic particles prepared by the process of our invention is in the preparation of composite magnetic ion exchange

5 resins. Beads comprising the cross-linked styrene polymer of our process can be converted to resins by processes such as chloromethylation and sulphonation with chlorosulphonic acid or oleum without significant attack on the magnetic particles incorporated into the  
10 beads. There has previously been no satisfactory process for such composite resins.

Other particulate matter may be incorporated into the polymer beads of our invention in addition to magnetic particles. For example, there may be added  
15 weighting agents such as zircon and other minerals, pigments, and fillers of various types.

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The invention is now illustrated by, but not limited to, the following examples:

Example 1

Preparation of polymeric dispersant

- 5           A mixture of styrene (90 g), 4-vinylpyridine (10 g), and benzoyl peroxide (1.27 g) was added dropwise to toluene (100 ml; nitrogen purged) over 3 hours at 100°C. The solution was then refluxed for 4-5 hours until a golden-coloured copolymer was obtained. The co-  
10 polymer is stable to air but will thicken if left standing for longer periods.

Example 2

The procedure of Example 1 was repeated except that the quantity of 4-vinylpyridine was 20 g.

15 Example 3

The procedure of Example 1 was repeated except that the quantity of styrene was 100 g and the 4-vinylpyridine was replaced by an equal weight of vinyl-trimethoxysilane.

20 Example 4

Pre-coating of magnetic particles

- A sample of Bayer S11  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was coated with the styrene/4-vinylpyridine copolymer of Example 1 by re-fluxing the sample in xylene with 6.25% of its weight of  
25 copolymer. The xylene was then removed by distillation.

Examples 5 and 6

The procedure of Example 4 was repeated using, respectively, the copolymers of Examples 2 and 3.

Example 7

30 Preparation of coated magnetic particles

A mixture of the pre-treated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (52 g) of Example 4, styrene (52 g), divinylbenzene (10 g), and the styrene/4-vinylpyridine copolymer (10 g) of Example 1

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was glass-ball milled for about 6 hours at ambient temperature. Benzoyl peroxide (1.0 g) was then added and the milling continued for 1 hour. The mixture was decanted from the glass balls and added to an aqueous suspension containing polyvinyl alcohol (500 g of 10.76% solution) dissolved in calcium chloride solution (600 mls; 40% aqueous solution).

The mixture was dispersed by vigorous stirring at 1500 rpm for about 15-20 minutes. At this stage the desired particle size (2-15 m) had been achieved and the stirring speed was reduced to 300 rpm. The temperature was raised to 80°C to complete the styrene/divinylbenzene polymerization (approximately 16 hours).

The suspension was then diluted with hot water and the coated particles were separated from the polyvinyl alcohol solution by centrifugation, followed by several successive hot-water washings and centrifugations to remove adhering solution. The coated particles were finally washed with ethanol and acetone and recovered by filtration.

#### Examples 8 and 9

The procedure of Example 7 was repeated using, respectively, the coated particles of Examples 5 and 6, and in each case the polymeric dispersant was that previously used to pre-coat the particles. If the polymeric dispersant was omitted during this coating procedure, some of the magnetic particles were "flushed" from the polymerizing beads and remained partly or completely uncoated and unprotected after the polymerization reaction was complete.

#### Example 10

The coated particles of Example 7 were suspended in glacial acetic acid and the weight loss measured at various time intervals to determine the extent of attack on the magnetic material by the acid medium. The results

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are tabled below together with data from a comparison experiment with a sample of the magnetic material that had not been given a protected coating.

Loss of  $\text{Fe}_2\text{O}_3$  (% w/w)

Sample	Days					
	1	6	14	22	30	82
Unprotected $\gamma\text{-Fe}_2\text{O}_3$	0.27	0.45	0.64	0.93	1.0	1.8
Protected $\gamma\text{-Fe}_2\text{O}_3$ (Example 7)	0.11	0.12	0.14	0.16	0.30	0.29

5. Similar protection against attack by acetic acid was found with the protected particles of Examples 8 and 9.

Example 11

Preparation of beads comprising  $\gamma$ -ferric oxide

- 10 A mixture of the pre-treated  $\gamma\text{-Fe}_2\text{O}_3$  (47 g) of Example 4, styrene (69.6 g), divinylbenzene (9.4 g), and the styrene/4-vinylpyridine copolymer (4.0 g) of Example 1 was glass-ball milled for about 4½ hours at ambient temperature. Benzoyl peroxide (1.0 g) was then added
- 15 and the milling continued for 1 hour. The mixture was decanted from the glass balls and added to an aqueous suspension containing polyvinyl alcohol (400 g of 10.76% solution) dissolved in calcium chloride solution (600 mls; 23.0 aqueous solution).

- 20 The mixture was dispersed by vigorous stirring at 250 rpm for about 15-20 minutes. At this stage the desired bead size (50-500  $\mu\text{m}$ ) had been achieved and the

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stirring speed was reduced to 100 rpm. The temperature was raised to 80°C to complete the styrene/divinylbenzene polymerization (approximately 16 hours).

The suspension was then diluted with hot water and the coated beads were separated from the polyvinyl alcohol solution by sieves, followed by several successive hot-water washings. The coated beads were finally washed with ethanol and acetone and recovered by filtration.

10 Example 12

Preparation of beads comprising chromium dioxide

Styrene-4-vinylpyridine copolymer (12.6 g) was dissolved into styrene (111 g) and divinylbenzene (7.80 g) monomers. To the monomer mixture was added 15 CrO<sub>2</sub> (60 g) and the composite was glass-ball milled for 6 hours. Benzoyl peroxide (1.0 g), as an initiator was added to the mixture and further milled for 1 hour. The glass beads were then separated by filtering the monomer content through a coarse sieve. The filtrate was 20 dispersed into a previously prepared aqueous suspension containing polyvinyl alcohol (PVA) (600 g, of 10.76% solution) dissolved in 900 ml of a 30% calcium chloride solution.

The composite was dispersed at 200 rpm until the 25 desired bead size of 150-200 µm was obtained. The stirrer speed was then reduced to 100 rpm and the aqueous suspension was heated to 77-80°C (internal) or 90° (external temperature) to initiate the polymerization.

The suspension was diluted with some hot water 30 and the CrO<sub>2</sub> beads were collected by pouring the content through a very fine sieve (usually 100 µm sieve) and washing the beads with copious amounts of warm water to remove any residual PVA on the beads. They were then transferred to a large sintered funnel and further washed 35 with ethanol and with acetone.

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Example 13Preparation of beads comprising zircon/chromium dioxide (1:1)

Styrene-4-vinylpyridine copolymer (48.7 g) was  
5 dissolved into styrene (333 g) and divinylbenzene  
(23.6 g) monomers. To the monomer mixture was added  
 $\text{CrO}_2$  (130 g) and  $\text{ZrSiO}_4$  (130 g) and the composite was  
glass-ball milled for 6½ hours. Benzoyl peroxide  
(3.0 g), as an initiator was added and milled into the  
10 mixture for another 1 hr. The glass beads were then  
separated from the monomer mixture by filtration using  
a coarse sieve. The filtrate was dispersed into a  
previously prepared aqueous suspension containing PVA  
(2 000 g, of an 8.75% solution) dissolved in 2 500 g of  
15 a 21.6% calcium chloride solution.

The composite was dispersed at 250 rpm until  
the desired bead size of 250-700  $\mu\text{m}$  was obtained. The  
stirrer speed was then reduced to 100 rpm and the  
aqueous suspension heated to 77-80°C (int) or 90°C  
20 (ext) to initiate the polymerization.

Fairly firm beads were obtained after 2 hours,  
but left for 16 hours to complete the polymerization.  
The aqueous suspension was diluted with some hot water  
and the  $\text{CrO}_2/\text{ZrSiO}_4$  beads were filtered through a fine  
25 sieve (100  $\mu\text{m}$  sieve) and the collected beads washed  
with copious amounts of warm water to remove residual  
PVA adhering on the beads. The beads were then trans-  
ferred to a large sintered funnel and further washed  
with ethanol and then with acetone.

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## CLAIMS

1. A process of incorporating non-polymeric particulate matter into a polymeric matrix which process comprises dispersing the non-polymeric particulate matter by a polymeric dispersant which is a copolymer prepared from a first component consisting of at least one monomer selected from the group consisting of vinyl aromatic hydrocarbons, and a second component consisting of at least one monomer selected from the group consisting of tertiary-nitrogen-containing vinyl monomers and vinyl-trialkylloxysilanes, in a medium comprising an organic phase comprising one or more vinyl monomers selected from the group consisting of styrene, substituted styrenes, and vinyltoluenes, and an aqueous phase containing a suspension stabilizer, and a cross-linking agent followed by the addition of a polymerization initiator.
2. A process according to claim 1 wherein the non-polymeric particulate matter comprises magnetic particles.
3. A process according to claim 2 wherein the magnetic particles are selected from the group consisting of ferrites and chromium dioxide.
4. A process according to claim 2 or 3 wherein the non-polymeric particulate matter comprises zircon.
5. A process according to any one of claims 1 to 4 wherein the non-polymeric particulate matter comprises  $\gamma$ -iron oxide and zircon.
6. A process according to any one of claims 1 to 5 wherein the said first component is a substituted styrene.
7. A process according to any one of claims 1 to 5 wherein the said first component is styrene.



8. A process according to any one of claims 1 to 7 wherein the said second component is selected from the group consisting of 2-vinylpyridine, 4-vinylpyridine, methyl dimethylaminomethacrylate, vinyltrimethoxysilane, and vinylthriethoxysilane.

9. A process according to any one of claims 1 to 5 wherein the said copolymer is selected from the group consisting of styrene/2-vinylpyridine, styrene/4-vinylpyridine, and styrene/vinyltrimethoxysilane.

10. A process according to any one of claims 1 to 9 wherein the copolymer contains from 80 to 97% w/w of the said first component and the balance is the said second component.

11. A process according to any one of claims 1 to 10 wherein the weight ratio of non-polymeric particulate matter to the polymeric dispersant is in a range from 12:1 to 5:1 and the weight ratio of polymeric dispersant to vinyl monomers is in a range from 1:5 to 1:20.

12. A process according to any one of claims 1 to 11 wherein the suspension stabilizer is polyvinyl alcohol.

13. A process according to any one of claims 1 to 12 wherein the weight ratio of organic phase to organic phase is in a range from 1:5 to 1:20.

14. A process according to claim 13 wherein the weight ratio of organic phase to aqueous phase is in a range from 1:10 to 1:16.

15. A process according to any one of claims 1 to 14 wherein the crosslinking agent is divinylbenzene.

16. A process according to any one of claims 1 to 15 wherein the non-polymeric particulate matter is coated with polymeric dispersant prior to the addition of vinyl

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monomers and crosslinking agent.

17. Polymeric beads in a size range from 1 to 1 000  $\mu$ m comprising non-polymeric particulate matter and prepared by the process of any one of claims 1 to 16.

18. Polymeric beads according to claim 17 wherein the non-polymeric particulate matter comprises magnetic particles.

19. Polymeric beads according to claim 18 wherein the non-polymeric polymeric matter comprises a weighting agent.

20. Polymeric beads according to claim 19 wherein the weighting agent is zircon.

# INTERNATIONAL SEARCH REPORT

00539/8

International Application No PCT/AU80/00018

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.<sup>3</sup> C08F 2/44, 212/08, 292/00

## II. FIELDS SEARCHED

Minimum Documentation Searched \*

Classification System	Classification Symbols
IPC	C08F 2/44, 292/00, 1/84, 1/86
US Cl.	260/42.53

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

AUSTRALIAN CLASSIFICATION 09.4-33, 09.4-35, 09.4-37

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>14</sup>

Category *	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>16</sup>
X	AU, B, 439,432, published 1971, May 20, see pages 17-21, Dulux Aust. Ltd.	1, 6-20
X	AU, B, 493,973, published 1976, November 25, see page 4 last line, page 65 (Ex. 24), page 67 (Ex. 31), page 72 and page 82, ICI Ltd.	1-23
X	US, A, 3,884,871, published 1975, May 20, see column 2 lines 33-34, column 4 line 30, column 5 lines 2-5, Example 4 and claim 1, D.F. Herman and D. Simone	1, 6-20
X	GB, A, 1,407,257, published 1975, September 24, see Examples 1, 11, 12, 20, 23, 29, 34 and 49, Bayer AG	1, 6-20
X	SU, A, 476-279, published 1975, November 13, A.N. Bolotov	1, 6-20
X	SU, A, 496-287, published 1976, December 3, B.N. Laskorin	1, 6-20

### \* Special categories of cited documents: <sup>18</sup>

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

## IV. CERTIFICATION

Date of the Actual Completion of the International Search \*

23 JULY 1980 (23/07/80)

Date of Mailing of this International Search Report \*

30 JULY 1980 (30-07-80)

International Searching Authority \*

AUSTRALIAN PATENT OFFICE

Signature of Authorized Officer <sup>19</sup>

A W WINCH

*[Signature]*

# INTERNATIONAL SEARCH REPORT

International Application No PCT/AU80/00018

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) <sup>2</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl. <sup>3</sup> C08F 2/44, 212/08, 292/00

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>4</sup>

Classification System	Classification Symbols
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US Cl.	260/42.53

Documentation Searched other than Minimum Documentation  
to the extent that such Documents are Included in the Fields Searched <sup>5</sup>

AUSTRALIAN CLASSIFICATION 09.4-33, 09.4-35, 09.4-37

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>11</sup>

Category <sup>6</sup>	Citation of Document, <sup>12</sup> with indication, where appropriate, of the relevant passages <sup>13</sup>	Relevant to Claim No. <sup>14</sup>
X	AU, B, 439,432, published 1971, May 20, see pages 17-21, Dulux Aust. Ltd.	1, 6-20
X	AU, B, 493,973, published 1976, November 25, see page 4 last line, page 65 (Ex. 24), page 67 (Ex. 31), page 72 and page 82, ICI Ltd.	1-23
X	US, A, 3,884,871, published 1975, May 20, see column 2 lines 33-34, column 4 line 30, column 5 lines 2-5, Example 4 and claim 1, D.F. Herman and D. Simone	1, 6-20
X	GB, A, 1,407,257, published 1975, September 24, see Examples 1, 11, 12, 20, 23, 29, 34 and 49, Bayer AG	1, 6-20
X	SU, A, 476-279, published 1975, November 13, A.N. Bolotov	1, 6-20
X	SU, A, 496-287, published 1976, December 3, B.N. Laskorin	1, 6-20

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"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

## IV. CERTIFICATION

Date of the Actual Completion of the International Search <sup>16</sup>

23 JULY 1980 (23/07/80)

Date of Mailing of this International Search Report <sup>17</sup>

30 JULY 1980 (30-07-80)

International Searching Authority <sup>18</sup>

AUSTRALIAN PATENT OFFICE

Signature of Authorized Officer <sup>19</sup>

A. W. WINCH

01959 D/02 A97 J01 (A13A14) CSIR 08.06.79  
COMMONWEALTH SCI/IND ORG (ICIL) \*WP 8002-687  
08.06.79-AU-009114 (11.12.80) C08f-02/44 C08f-212/08 C08f-292  
Incorporating non-polymer particles into polymer matrix - using  
polymer dispersant in vinyl monomers and crosslinker and adding  
polymerisation initiator

Incorporation of non-polymeric particles (I) into a polymer matrix is carried out by dispersing (I) using a polymeric dispersant in a medium of vinyl monomers and crosslinker, followed by adding a polymerisation initiator. Pref. polymerisation is effected using a vinyl monomer org. phase and aq. phase contg. suspension stabiliser, pref. PVA, the wt. ratio of org. to aq. phase is 1:5-20, pref. 1:10-16. Polymer beads of size 1-1000 micron contg. (I) are formed.

#### Uses/Advantages

Incorporated in the polymer beads is resistant to chemical attack and the beads may form composite adsorbents and ion exchange resins.

#### Materials

Pref. (I) is magnetic particles, esp. ferrites and/or dioxides or gamma-iron oxide and silicon as weighting agent. Pref. dispersant is a copolymer of (a) vinyl aromatic cpd., esp. (subd.) styrene and (b) tert. N contg. vinyl monomer and/or vinyltrialkoxysilanes, esp. 2- or 4-vinyl pyridine, methyl dimethylaminomethacrylate or vinyltri(methoxysilane). (a) is present in amt. of 80-97 wt. % of the copolymer. Pref. vinyl monomer is (subd.) styrene or vinyltoluene. Pref. crosslinker is divinylbenzene.

A(4-A, 4-C1, 4-D1, 8-S, 10-B5, 11-A3, 12-E8) J(1-D1, 1-D4).

#### Details

Pref. wt. ratio of (I) to dispersant is 12-5 : 1 and wt. ratio dispersant to vinyl monomers is 1 : 5-20. (I) is pref. coated with the dispersant prior to adding the vinyl monomers and crosslinker.

#### Example

Layer 811 (RTM; gamma Fe<sub>2</sub>O<sub>3</sub>) was coated with a styrene-4-vinyl pyridine copolymer by refluxing in xylene with 6.25 wt. % of copolymer, xylene being removed by distillation. 52 g of the pretreated gamma Fe<sub>2</sub>O<sub>3</sub>, 10 g divinylbenzene and 10 g of the above styrene-4-vinylpyridine copolymer was ball milled for 6 hr. 1.0 g benzoyl peroxide was added and milling continued for 1 hr. The obd. mixt. was added to 500 g of a 10.76% soln. of PVA, dissolved in 600 ml of a 40% aq. CaCl<sub>2</sub> soln. The mixt. was dispersed by stirring to obtain particles of the desired size (3-15 micron). The temp. was raised to 80 deg. C to complete the styrene-divinylbenzene prepn. The suspension was diluted with hot water, the coated particles were separated by centrifuging, hot water washed and further centrifuged. The particles were finally washed with ethanol and acetone and filtered.

Full Patentees: ICI Australia Ltd.; Commonwealth Scientific and Industrial Research Organisation.